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<b>(21) International Application Number:</b> PCT/US89/05666 <b>(22) International Filing Date:</b> 18 December 1989 (18.12.89) <b>(30) Priority data:</b> 285,817 16 December 1988 (16.12.88) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 285,817 (CIP) Filed on 16 December 1988 (16.12.88) <b>(71) Applicant (for all designated States except US):</b> HYPERION CATALYSIS INTERNATIONAL [US/US]; 128 Spring Street, Lexington, MA 02173 (US).	<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> MANDEVILLE, W., Harry [US/US]; 7 Pillings Pond Road, Lynnfield, MA 01940 (US). TRUESDALE, Larry, K. [US/US]; 148 Crossbow Lane, North Andover, MA 01845 (US). <b>(74) Agent:</b> FRENCH, Timothy, A.; Fish & Richardson, One Financial Center, Suite 2500, Boston, MA 02111-2658 (US). <b>(81) Designated States:</b> AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> CARBON FIBRILS AND A CATALYTIC VAPOR GROWTH METHOD FOR PRODUCING CARBON FIBRILS  <b>(57) Abstract</b>  A process for preparing carbon fibrils by contacting a source of carbon with a supported catalyst that includes at least one multivalent transition metal having a size of about 35 to 700 Å deposited on an inorganic substrate having a size of up to about 400 microns.		

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CARBON FIBRILS AND A CATALYTIC VAPOR GROWTH METHOD  
FOR PRODUCING CARBON FIBRILS

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This invention relates to fibrils. It more particularly refers to carbon/graphite fibrils and to an improved process for producing such. Carbon fibrils as used herein means  
5 graphitic fibrils having high surface area, high Young's modulus of elasticity and high tensile strength which are grown catalytically from available sources of carbon.

This application is a continuation-in-part of Application Serial No. 149,573, filed January 8, 1988.

10 Background of the Invention

It has been known for some time that one could make fibrils by decomposing various carbon contributing molecules, such as light hydrocarbons, in contact with a suitable metal catalyst, such as for example iron alone or in combination  
15 with other metals. In the past, the fibrils which have been made have been somewhat thicker than desirable and/or have been burdened with an overcoat of thermally deposited generally amorphous carbon which tended to reduce the desirable physical properties thereof or have been made in  
20 poor yields. Prior workers have sought to ameliorate the disadvantages of the amorphous carbon overcoating by subjecting the finished fibril to a very high temperature graphitizing treatment whereby generally rendering the fibrils of substantially greater cross

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sectional consistency from both a composition and a crystallinity point of view.

It is obvious that the improved fibril properties engendered by this high temperature graphitization process are expensive, because high temperature treatments are expensive. Additionally, such graphitized fibrils may still be too thick for many purposes because, graphitizing does not significantly reduce the fibril diameter. Thus, it is desired to produce high yields of high quality fibrils, preferably thin fibrils, which, in a preferred aspect of this invention, do not need post production graphitization.

#### Summary of the Invention

More particularly refers to carbon/graphite fibrils and to an improved process for producing such. Fibrils are made according to this invention in a high temperature, catalytic process. The Fibril can be made of a variety of materials, e.g. carbon, silicon nitride, silicon carbide, etc. In one important embodiment, such fibrils have the atoms in their composition relatively ordered at their outer surfaces as they are made by this process. Thus, it can be said that this process preferably directly produces a product having a relatively crystalline outer region for substantial portions of its length and may have inner regions where its atoms are less ordered. It may, and often does, even have a hollow region axially positioned along substantial portions of its length.

Fibrils according to this invention are characterized by small diameters, e.g. about 35 to 70 nanometers and high L/D up to about 100 and even more. Where the preferred structure described above is produced, it is suitably produced directly in the fibril forming process without further processing being required.

Where the fibrils of this invention are to be made of carbon, such can be produced in quite high yields. In this embodiment, a suitable source of carbon may be a hydrocarbonaceous material illustrated by:

5 methane, ethane, propane, butane, benzene, cyclohexane, butene, isobutene, ethylene, propylene, acetylene, toluene, xylene, cumene, ethyl benzene, naphthalene, phenanthrene, anthracene, formaldehyde, acetaldehyde, acetone, methanol, ethanol, carbon monoxide, other  
10 similar materials, and mixtures of two (2) or more thereof. Such feed is contacted with a suitable catalyst at elevated, fibril forming temperatures for a time sufficient to cause graphitic carbon fibrils to grow.

15 It is within the scope of this invention to provide a non-hydrocarbonaceous gas along with the carbon contributing reactant. Such gas might for example be hydrogen or carbon monoxide. Inert diluents are also suitable.

20 The temperature of the process of this invention can vary widely depending upon the nature of the carbon source being used, however, for best results, it should be kept below the thermal decomposition temperature thereof. In the case of using a mixture of  
25 such carbon sources, the operating temperature should be maintained below the thermal decomposition temperature of the most temperature-sensitive carbon source in the system. Temperatures in the range of 500 to 1500°C may be found to be generally usable, depending on the carbon  
30 source used, preferably between about 600 and 900°C.

Subatmospheric, atmospheric and/or super atmospheric pressures may be used as dictated by other processing considerations. It has been found that it is desirable to provide the carbon source in the vapor

state, and thus, the pressure should not be so high as to cause the carbon source to be in the liquid state under fibril forming temperature conditions. Further, it is desirable although not essential to provide a suitable gaseous diluent, such as hydrogen or inert gases, for example, nitrogen.

It is preferred that the system as a whole be non-oxidizing wherefor preferably avoiding the presence of oxygen if practical. Small amounts of these materials can be tolerated. It should be understood that the existence of oxidizing conditions, at the elevated temperatures operative for this process, will cause oxidation of the carbon source and therefor reduce the amount of carbon from such source which is available for conversion into fibrils as desired.

It may be desirable to provide suitable heat to this reaction system where and when needed. Temperature of different parts of the reactor zone may be suitably controlled to different temperatures and this is easily accomplished by using electrical resistance heating. However in larger scale industrial practice, electric resistance heating may sometimes be economically replaced by direct heating, such as for example by burning some of the carbon contributing feed to raise the temperature of the remainder of the feed, or by feeding the catalyst or the carbon contributing feed, or the diluent into the system at a sufficiently elevated temperature such that direct heat exchange of the component with each other will cause the fibril forming reaction to proceed as desired.

The nature of the catalyst seems to have a significant effect upon the yield of fibrils produced according to this invention. It is known to use iron group metals such as iron, cobalt or nickel to catalyze

the conversion of carbon contributing compounds to fibrils, and such metals are within the scope of this invention. In addition, many other multivalent transition metals, including lanthanides, appear to be operative. Particularly useful catalytic metals include inter alia: iron, molybdenum cobalt, nickel, platinum, palladium, vanadium, and chromium. Of specific interest in this process are certain combinations of transition metals. Particularly useful combinations include iron and molybdenum, iron and chromium, copper and nickel, iron and platinum, iron and tin, iron and nickel, iron and manganese, and iron and cerium.

The yield of fibrils produced according to the practice of this invention appears to be related to the physical state of the catalyst used to produce such. According to this invention, it is important that the multivalent transition metal fibril forming catalyst be present on a suitable substrate as relatively discrete catalytic sites, each about 35 to 700A preferably 60 to 300A in size during fibril formation. These relatively discrete catalytic sites are produced by suitably applying the transition metal (in an appropriate state) to a substrate, suitably an inorganic substrate material which can include carbon/graphite.

The size of the substrate particle is a matter of some importance dependent upon the engineering of the process itself. For example, if the fibril formation is to take place in a fluid bed type of reaction zone, the substrate particle size will suitably be less than about 400 microns. If the fluid bed is an evullient bed of catalyst particles, particle sizes of about 50 to 300 microns have been found to be preferable. If the fluid bed is an evullient bed of fibrils containing small amounts of catalyst particles, i.e. up to about ten

percent, these should preferably have a size of about 1 to 100 microns. If the fluid bed is a transport bed, either up flow or down flow, the catalyst carrying particles will suitably be less than about 10 microns, preferably less than about one micron.

It has been found that depositing one or more suitable transition metals on small particle substrates produces a catalyst well suited to use in this invention. The substrate is a material which can conveniently withstand the rigors of fibril formation conditions, e.g. temperatures of about 500 to 1500°C. Suitable substrates include carbon, graphite, inorganic oxides, etc. The particular substrate will be matched to the particular transition metal(s) catalyst such that the metal is bound strongly enough to retard migration and agglomeration but not so strongly as to prevent or retard the transition metal from catalyzing fibril formation. Illustrative, inorganic oxides include alumina, silica, magnesia, silicates, aluminates, spinels etc. Mixtures can be used.

Thus, very small particle iron, such as might be produced by decomposition of iron compounds, can be deposited on very small particle alumina, e.g. fumed alumina having particle sizes of no larger than about 100 mesh. These alumina particles may be made up of individual crystallites which are on the order of about 50 to 200 Å, which agglomerate to form particles having substantial available surface area sufficient to receive deposits of appropriately sized transition metal catalyst.

The substrate particles are suitably less than about 300 microns. They may be less than 1 micron in transport bed use. It appears that the transition metal reacts with the substrate crystallites such as to bond



the metal to the substrate and fix its position, so as to prevent or retard catalyst agglomeration, at least for so long as it takes to contact the supported transition metal with the suitable carbon source at appropriate reaction conditions. Upon contact, the carbon source seems to pyrolyze on the catalytic site and the desirable morphology fibril grows therefrom.

As noted, the state of the transition metal catalyst site during fibril formation is important to the practice of this invention. Sometimes, it appears that this desirable catalytic site state as well as the state of the substrate carrier therefore is changing during the whole process hereof. Thus, the catalytic sites may agglomerate or disperse to some extent during the period from introduction into the reaction zone until the fibrils made by the process are recovered. At the time the fibrils are recovered, particles of transition metal catalyst which are sometimes recovered with the fibrils are of about 35 to 700A, preferably 60 to 300A in size. Thus, it is believed that the size of the active catalyst site during fibril formation is substantially comparable to the diameter of the fibril being formed.

It appears that as fibril formation takes place, active catalyst sites become catalytically expended and need to be replaced. Additionally, it has been found that the fibril forming process is more efficient and capable of better control if the catalyst is added to the reaction zone intermittently or continuously over substantially the entire course of the reaction, or at least a substantial portion thereof. It is possible that the catalyst containing substrate of this invention may ablate with use. That is, when a fibril is formed on a particular catalytic site, that

fibril and its associated site may break off from the substrate, with or without some of the substrate, thereby exposing further catalytic sites which were previously inside the substrate particle. Thus, periodic or continuous addition of fresh catalyst is desirable

Thus, according to this invention, the fibril forming process hereof is preferably substantially continuous in that a suitable source of carbon, with or without carrier gas, and catalyst containing particles are continuously or intermittently fed to a reaction zone maintained at a fibril forming temperature appropriate to the carbon source being used; while fibril product, usually admixed with the remnants of the catalyst and sometimes substrate as well, are continuously or intermittently recovered.

The transition metal may be deposited on the substrate by any commonly used technique for accomplishing such deposition. Vapor deposition, sputtering and impregnation may all be suitable. In particular, it has been found to be expeditious to form a water solution or dispersion of the desired metal or metals, mix the water phase with appropriately sized substrate, and then precipitate the metal(s) onto the substrate, e.g. by evaporating the water or any other conventional means.

It is also within the scope of this invention to deposit the desired transition metal(s) from an organic (as opposed to aqueous) medium. Suitably the transition metal can be dissolved or suspended in such medium, for example, as an organometallic compound, and then impregnated onto and into a suitable substrate. The organic carrier medium is removed, leaving behind the impregnated, deposited transition metal.

After the transition metal is combined with the substrate as aforesaid, it may be important to treat this combination so as to activate it for this particular catalytic purpose, e.g., by heating it to separate the metal from other ligands, if any, in the deposition compound. It may also be necessary to adjust the size of the prepared catalyst to make it suitable for use in this invention. Comminution or agglomeration, e.g. by binding, may be desirable to produce particles of the proper size, i.e. of less than about 400 microns.

The catalyst of this invention may be put on the substrate hereof in any form or chemical oxidation state. It may be the oxide or have some other ligand. It may be reduced prior to use, but this is not necessary since the fibril forming reaction is a reducing environment and thus the transition metal will be reduced during, or immediately prior to, fibril forming use.

Fibrils which are very thin and long, diameters of about 3.5 to 70 nanometers and L/D of up to 100 or more, are produced using these catalysts. These fibrils, as produced by this process, without the necessity of further treatment, and without the coproduction of a thermal carbon overcoat, comprise a carbon layer generally concentric about an axis which comprises multiple essentially continuous layers of ordered carbon atoms, which preferably and usually are crystalline and graphitic. This, as produced, outer layer of ordered carbon atoms often surrounds an inner layer of less ordered carbon atoms. Most preferred products of this invention are high yields of high quality, thin fibrils of appropriate long length having substantially uniform, concentric, substantially

continuous, ordered, multiple layers of carbon about an axial (inner core) region, which has a different composition/crystallinity and is preferably hollow. Such fibrils preferably have up to about 100 times, and more greater length than diameter, have diameters of up to about 700 angstroms and are substantially cylindrical graphite about a substantially hollow core as made and without having been treated at higher temperatures than the original fibril manufacturing temperature.

According to one aspect of this invention, operating with catalyst particles as herein set forth, yields of fibrils of greater than about 30 times the weight of transition metal in the catalyst are achievable. In many cases, particularly with mixed transition metals, yields of between 100 and 200 times the weight of transition metal in the catalyst have been achieved. It has been found that in comparable processes, combinations of transition metal catalysts have sometimes increased yields by a factor of as much as 2 or even more.

The following examples illustrate the practice of this invention. By following one or more of these examples, high yields of unique fibrils as above described are produced.

#### Example 1

A catalyst was prepared using Degussa fumed alumina with an average particle size of about 100A and an aggregate mesh size of -100. Iron acetylacetonate was deposited on these alumina particles in a ratio of about 1 part iron, as the acetylacetonate, to 10 parts by weight of alumina. The resultant particle was heated under a hydrogen/ethylene atmosphere under reaction conditions.

A one (1) inch tube was heated to about 650°C while it was being purged with argon. A mixed flow of hydrogen, at 100 ml/min, and ethylene, at 200 ml/min, was fed to the hot tube for five minutes whereupon catalyst was introduced into the reactor tub. The ethylene/hydrogen mixture was continued through the tubular reactor for 0.5 hours after which the reactor was allowed to cool to room temperature under argon. Harvesting of the fibrils so produced showed a yield of greater than 30 times the weight of the iron in the catalyst.

#### Example 2

Into a 3 L. round bottom flask was added 80.08 g of Degussa fumed alumina and 285 ml of methanol. The mixture was stirred to produce a thick paste before a solution of 78.26 g (0.194 moles) of ferric nitrate nonahydrate and 4.00 g (0.0123 moles) of molybdenum(VI) oxide bis(2,4-pentanedionate) in 300 ml of methanol (Fe to Mo atom ratio of 94:6) was added slowly. The thick paste which had collected on the sides of the flask was washed down with 65 ml of additional methanol and the mixture was stirred for 1 hour before house vacuum (28 in. Hg) was applied while stirring overnight. The purple-tinted solid was placed in a vacuum (28 in. Hg) oven at 100°C for 29 hours. A total of 100.7 g of catalyst was obtained. The catalyst was ground and passed through an 80 mesh sieve prior to use. Analysis of the catalyst indicated 9.43% by weight iron and 0.99% by weight molybdenum.

A vertical furnace containing a 1 inch quartz tube with an internal quartz wool plug and thermocouple was equilibrated at 650°C under a down flow of 100 ml/min. hydrogen and 200 ml/min. ethylene. Into the tube (onto the quartz wool plug) was added 0.1044 g of

the above-described catalyst. After 30 min., the hydrogen/ethylene flow was stopped and the oven was allowed to cool to near room temperature. A total of 1.2434 g of fibrils was harvested for a yield ratio of 126 times the iron weight content of the catalyst.

### Example 3

A sample of catalyst from example 2 (1.6371 g) was placed in a horizontal furnace under argon and was heated to 300°C. After 30 min. at this temperature, the furnace was cooled and 1.4460 g of catalyst was recovered (12% wt. loss), having 11.1% by weight iron and 1.2% by weight molybdenum.

A vertical tube furnace containing a 1 in. quartz tube with an internal quartz wool plug and thermocouple was equilibrated at 650°C under a 100 ml/min. down flow of hydrogen and 200 ml/min. down flow of ethylene. Into the hot tube was added 0.1029 g of the catalyst described above. After 30 min., the hydrogen/ethylene flow was stopped and the oven was allowed to cool to near room temperature under argon. A total of 1.3750 g of fibrils was isolated for a weight yield based on theoretical iron content of 120 times the iron content.

### Example 4

The vertical tube furnace described in Example 2 was equilibrated at 700°C under the flow of 100 ml/min. hydrogen and 200 ml/min. propane. Onto the quartz wool plug was added 0.1041g of catalyst from Example 2. After 30 min. the fuel gases were stopped and the product was cooled under argon. A total of 0.3993 of fibrils was isolated for a weight yield of 41 times the catalyst iron content.

Example 5

The procedure of Example 4 was followed at 650°C using 0.1004 g of catalyst from Example 2. A total of 0.3179 g of fibrils was harvested for a weight yield of 34 times the iron content of the catalyst.

Example 6

Into a round bottom flask was added 4.25 g of Degussa fumed alumina and 30 ml of methanol. The mixture was mechanically stirred while a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 0.51 g (1.56 mmol) of molybdenum(VI)oxide bis(2, 4-pentanedionate) in 50 ml of methanol was slowly added. The mixture was stirred for 1 hour before the solvent was removed with the aid of a rotary evaporator. The resulting damp solid was vacuum dried at 105°C, 28 in. Hg for 18 hours. The resulting catalyst was ground and passed through an 80 mesh sieve. A total of 5.10 g of catalyst was obtained. Analysis of the catalyst indicated 9.04% by weight iron and 2.18% by weight molybdenum to be present.

Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0936 g of the above catalyst. A total of 0.9487 g of fibrils was isolated for a weight yield of 126 times the catalyst iron content.

Example 7

Into a round bottom flask was added 3.80 g of Degussa fumed alumina and 30 ml of methanol. The mixture was mechanically stirred while a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 2.04 g (6.25 mmol) of molybdenum(VI)oxide bis(2, 4-pentanedionate) in 100 ml of solvent was added. The mixture was held at 105°C and 28 in. Hg for 17 hrs. The dried catalyst was sieved (80 mesh) to produce 6.10 g of

powder. Analysis of the catalyst indicated 8.61% iron and 8.13% molybdenum by weight.

Fibrils were prepared following the procedure of Example 2 at 650°C using 0.1000 g of the above catalyst. A total of 0.8816 g of fibrils was isolated for a weight yield of 102 times the catalyst iron content.

#### Example 8

The procedure of Example 7 was followed at 700°C using methane and 0.1016g of catalyst. A total of 0.0717g of fibrils was isolated for a yield of 8.2 times the iron content of the catalyst.

#### Example 9

Into a 500 ml round bottom flask was placed 4.37 g of Degussa fumed alumina and 28 ml of methanol. To the stirred mixture was added a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 0.46 g (1.32 mmol) of chromium acetylacetonate in 75 ml of methanol. The mixture was stirred for 1 hr. before it was dried for 18 hr. at 105°C and 28 in. Hg. The catalyst was ground and sieved (80 mesh) to produce 5.57 g of powder. The theoretical metal content by weight was 11.9% iron and 1.4% chromium.

Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0976 g of the above catalyst. A total of 0.9487 g of fibrils was isolated for a yield of 82 times the theoretical iron content.

#### Example 10

Into a 500 ml round bottom flask was placed 4.40 g of Degussa fumed alumina and 35 ml of methanol. To the thick paste was added 4.32g (10.7 mmol) of ferric nitrate nonahydrate in 35 ml of methanol. The mixture was stirred for 45 min. before the solid was dried at 95°C and 28 in. Hg for 18 hr. The catalyst was ground and sieved (80 mesh).



Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0930 g of the above catalyst. A total of 0.4890 g of fibrils was isolated for a weight yield of 46 times the catalyst iron content.

5     Example 11

Into a round bottom flask was placed 4.33 g of Degussa fumed alumina in 30 ml of methanol. To the stirred paste was added a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 0.42 g (1.19 mmol) of ferric acetylacetonate in 50 ml of methanol. The mixture was stirred for 75 min. before drying at 105°C and 28 in. Hg for 17 hrs. The solid was ground and sieved (80 mesh) to yield 5.87 g of catalyst. Analysis showed 13.79% iron present in the catalyst.

15     Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0939 g of the above catalyst to produce 0.3962 g of fibrils. This corresponds to 31 times the iron content of the catalyst.

Example 12

20     Into a round bottom flask was added 4.33g of Degussa fumed alumina in 20 ml of water followed by a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 0.17g (1.38 mmol) of ammonium molybdate in 40 ml of water. The mixture was mechanically stirred for 1 hour. The water was removed at reduced pressure at 40°C overnight. Final drying was accomplished at 140°C and 26 mm. Hg for 21 hours to produce 5.57 g of solid. Analysis of the catalyst showed 9.87% by weight iron and 1.45% by weight molybdenum to be present.

30     Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0794 g of catalyst to produce 0.8656g of fibrils. This corresponds to 111 times the iron content of the catalyst.

Example 13

5 Into a round bottom flask, containing 4.33 g of Degussa fumed alumina and 30 ml of methanol, was added a solution of 4.33 g (10.7 mmol) of ferric nitrate nonahydrate and 0.16 g (0.368 mmol) of ceric nitrate in 50 ml of methanol. An additional 20 ml of methanol was used to wash all the salts into the flask. The mixture was stirred for one hour before the solvent was removed at reduced pressure. The solid was dried at 130°C and 27 mm Hg for four days to produce 5.32 grams of catalyst. Analysis of the solid indicated 9.40% iron and 0.89% cerium to be present.

10 Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0941g of catalyst to produce 0.7552g of fibrils. This corresponds to 88 times the iron content of the catalyst.

Example 14

15 Into a round bottom flask was added 4.33g of Degussa fumed alumina and 30 ml of methanol. Onto the alumina was poured a solution of 4.33g (10.7 mmol) of ferric nitrate and 0.31g (1.22 mmol) of manganese(II) acetylacetonate in 50 ml of methanol. The solvent was removed at reduced pressure (27 mm Hg) and the damp solid was vacuum dried at 140°C to produce 5.18g of solid. Analysis of the catalyst indicated 9.97% iron and 1.18% manganese.

20 Fibrils were prepared following the procedure of Example 2 at 650°C using 0.070g of catalyst to produce 0.4948g of fibrils. This corresponds to 66 times the iron content of the catalyst.

Example 15

25 Into a round bottom flask was added 4.33g of Degussa fumed alumina and 30 ml of methanol. Onto the alumina was poured a solution of 4.33g (10.7 mmol) of

ferric nitrate and 0.43g (1.22 mmol) of manganese(III) acetylacetonate in 50 ml of methanol. The solvent was removed at reduced pressure and the damp solid was vacuum dried at 140°C to produce 5.27g of solid.

5 Analysis of the catalyst indicated 10.00% iron and 1.18% manganese by weight.

Fibrils were prepared following the procedure of Example 2 at 650°C using 0.0723g of catalyst to produce 0.7891g of fibrils. This corresponds to 110  
10 times the iron content of the catalyst on a weight basis.

Example 16

Degussa fumed alumina (400g) and deionized water (8.0L) were added to a 22 L flask equipped with a stirrer, pH meter and probe, and two 2 L addition  
15 funnels. One funnel contained an aqueous solution of ferric nitrate nonahydrate (511g dissolved in 5654 ml of water) and the other an aqueous solution of sodium bicarbonate (480g dissolved in 5700 ml of water).

The pH of the alumina slurry was first adjusted  
20 to 6.0 by adding the sodium bicarbonate solution to raise it or the ferric nitrate solution to lower it. Next, both solutions were added simultaneously over 3-4 hours with good agitation while maintaining the pH at 6.0. When the addition was complete, stirring was  
25 continued for an additional 1/2 hour, after which the slurry was filtered on a 32 cm Buchner funnel. The filter cake was then washed with deionized water and returned to the 22 L flask. Next, additional deionized water was added and the slurry stirred for another 1/2  
30 hour. The batch was then filtered, washed with deionized water, and vacuum-dried at 100°C to constant weight (475g). Following drying, the final catalyst was prepared by grinding and sieving the product to -80 mesh.

Example 17

This Example illustrates the practice of this invention using periodic addition of catalyst to produce high fibril yields. A four-inch quartz tube, closed on the bottom, was placed in a 4 inch diameter x 24 inch long furnace. The tube was purged with argon while being heated to 620°C. When the tube was hot, the gas feed was switched to a mixture of hydrogen (1.0 l/min) and ethylene (5.6 l/min) via a dip tube to the bottom of the 4 inch tube. After 5 min of purging, the catalyst addition was begun.

A total of 41.13g of catalyst, prepared as described in the Example 16, was added to the hot reactor reservoir. The catalyst was added periodically to the hot reactor in small portions (0.2g) over a period of approximately 6 hours. After catalyst addition was complete, the reaction was allowed to run for an additional one hour and the reactor then cooled to room temperature under argon. The fibrils were removed from the tube and weighed. This batch gave 430g total yield of fibrils which is unusually high for a catalyst based upon iron has the only transitionmetal. In single batch addition fo an iron only catalyst, fibril yields of about 30 times the iron content have been observed whereas here the fibril yield is more than 70 times the iron content of the catalyst.

Example 18

The tube and furnace described in Example 17 were heated to 650° under an argon purge. When the tube was hot the gas feed was switched to hydrogen and ethylene as described in Example 17.

A total of 20.4g of catalyst (Fe-Mo) prepared as described in Example 2 was added in a manner similar to that described in Example 17. This batch gave a total fibril yield of 255g.

Claims

1           1. In the process of producing carbon fibrils  
2 by decomposing a source of carbon at elevated  
3 temperatures in contact with a multivalent transition  
4 metal and recovering the fibrils formed thereby; the  
5 improvement, whereby increasing the yield of such  
6 fibrils, which comprises contacting said source of  
7 carbon at a temperature of about 500 to 1500°C with a  
8 catalyst comprising at least one multivalent transition  
9 metal on an inorganic substrate having a size of up to  
10 about 400 microns, said metal being present on said  
11 substrate as a multiplicity of discontinuous catalytic  
12 sites which, at least during fibril formation, have a  
13 size of about 35 to 700°A which size is measured by  
14 measuring the size of transition metal particles  
15 recovered along with produced fibrils.

1           2. The improved process claimed in claim 1  
2 wherein said transition metal comprises iron with a  
3 catalyst site size of about 60 to 300A.

1           3. The improved process claimed in claim 1  
2 wherein said transition metal is iron mixed with at  
3 least one other transition metal.

1           4. The improved process claimed in claim 3  
2 wherein said other transition metal is at least one  
3 selected from the group consisting of molybdenum and  
4 chromium.

1           5. The improved process claimed in claim 1  
2 carried out at a temperature below the thermal  
3 decomposition temperature of the carbon source.

1           6. Th improved process claimed in claim 1  
2 wherein said carbon source is a mixture of hydrocarbons.

1           7. The improved process claimed in claim 1  
2 wherein said carbon source is at least one member  
3 selected from the group consisting of methane, ethane,  
4 propane, butane, benzene, butene, isobutene,  
5 cyclohexane, ethylene, propylene, acetylene, toluene,  
6 xylene, cumene, ethyl benzene, naphthalene,  
7 phenanthrene, anthracene, formaldehyde, acetaldehyde,  
8 acetone, methanol, ethanol and carbon monoxide.

1           8. The improved process claimed in claim 5  
2 including recovering a high yield of product comprising  
3 long, thin fibrils which, as produced, comprise at least  
4 long portions consisting essentially of ordered carbon  
5 atoms as their outer layer.

1           9. The improved process as claimed in claim 1  
2 carried out in an ebulliating bed wherein said  
3 catalyst/substrate has a particle size of about 50 to  
4 300 microns.

1           10. The improved process as claimed in claim 1  
2 carried out in a transport bed wherein said  
3 catalyst/substrate has a particle size of less than  
4 about 1 micron.

1 11. The improved process as claimed in claim 1  
2 including cofeeding said catalyst/substrate and said  
3 source of carbon downflow through a reaction zone.

1 12. The improved process claimed in claim 10  
2 including cofeeding said catalyst/substrate upflow  
3 through a reaction zone.

1 13. The improved process claimed in claim 1  
2 including cofeeding a non-hydrocarbonaceous gas with  
3 said carbon contributing feed.

1 14. The improved process claimed in claim 1  
2 including adding said catalyst particles to said process  
3 over the course of said fibril forming reaction.

1 15. A process for producing high yields of  
2 long, thin fibrils comprising at least long portions  
3 having atomically ordered outer surfaces, as made; which  
4 process comprises contacting a vaporous source of the  
5 atoms which will comprise said outer surface with a  
6 small particle substrate, having a size of up to about  
7 400 microns and having multiple discrete catalytic sites  
8 comprising at least one transition metal, at a  
9 temperature of about 500 to 1500°C but lower than the  
10 thermal decomposition temperature of said vaporous  
11 source of said atoms for a time sufficient to form  
12 fibrils; and recovering a product comprising said  
13 fibrils at least some of which have combined therewith  
14 at least one transition metal of a size of about 35 to  
15 700°A.

1 16. A process as claimed in claim 15 wherein  
2 said vaporous source comprises a mixture of a  
3 hydrocarbonaceous source of carbon and hydrogen.

1 17. A process as claimed in claim 16 wherein  
2 said transition metal comprises iron, said  
3 hydrocarbonaceous source of carbon is ethylene and said  
4 temperature is about 600 to 900°C.

1 18. A process as claimed in claim 16 wherein  
2 said transition metal is iron and molybdenum.

1 19. A process as claimed in claim 16 wherein  
2 said transition metal is iron and chromium.

1 20. A process as claimed in claim 16 wherein  
2 said transition metal is iron and cerium.

1 21. A process as claimed in claim 16 carried  
2 out in a fluidized bed.

1 22. A long, thin carbonaceous fibril made up  
2 of at least long portions comprising, as made and  
3 without having been subjected to temperature higher than  
4 about 1500°C, an outer layer substantially concentric  
5 about an axis consisting essentially of ordered carbon  
6 atoms.

1 23. A fibril as claimed in claim 22 comprising  
2 a substantially hollow core.

1 24. A fibril as claimed in claim 22 comprising  
2 an inner layer of carbon less ordered than said outer  
3 layer.

1 25. A multiplicity of fibrils comprising at  
2 least some fibrils as claimed in claim 22.



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/05666

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. 5 D01F 9/12 423/447.2																													
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; padding: 5px;">Classification System</th> <th style="border: 1px solid black; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">U.S.</td> <td style="border: 1px solid black; padding: 5px;">423/449,450,453,458,Dig.16, 447.1,447.2 428/408,367,398,376</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	U.S.	423/449,450,453,458,Dig.16, 447.1,447.2 428/408,367,398,376																							
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category <sup>9</sup></th> <th style="width: 60%; padding: 5px;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 30%; padding: 5px;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X Y</td> <td>US, A, 4,663,230 (TENNET) 05 May 1987 entire specification</td> <td style="text-align: center; vertical-align: top;">22-25 1-21</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>JAPAN 57-117,622 (ENDO) 22 July 1982 translated abstract</td> <td style="text-align: center; vertical-align: top;">1 to 25</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,767,737 (BROOKS) 30 August 1988 column 4, lines 1 to 69</td> <td style="text-align: center; vertical-align: top;">9-12,14 and 21</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,435,367 (PORTER et al) 06 March 1984 column 1, lines 49 to 55</td> <td style="text-align: center; vertical-align: top;">6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A P</td> <td>US, A, 4,816,289 (KOMATSU et al) 28 March 1989</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4,014,980 (FUJIMAKI et al) 29 March 1977</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4,650,657 (BROOKS) 17 March 1987</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 4,518,575 (PORTER et al) 21 May 1985</td> <td></td> </tr> </tbody> </table>			Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X Y	US, A, 4,663,230 (TENNET) 05 May 1987 entire specification	22-25 1-21	Y	JAPAN 57-117,622 (ENDO) 22 July 1982 translated abstract	1 to 25	Y	US, A, 4,767,737 (BROOKS) 30 August 1988 column 4, lines 1 to 69	9-12,14 and 21	Y	US, A, 4,435,367 (PORTER et al) 06 March 1984 column 1, lines 49 to 55	6	A P	US, A, 4,816,289 (KOMATSU et al) 28 March 1989		A	US, A, 4,014,980 (FUJIMAKI et al) 29 March 1977		A	US, A, 4,650,657 (BROOKS) 17 March 1987		A	US, A, 4,518,575 (PORTER et al) 21 May 1985	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Δ" document member of the same patent family</p> </div> </div>																													
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search   <b>26 FEBRUARY 1990</b> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report   <b>30 MAR 1990</b> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">           International Searching Authority   <b>ISA/US</b> </td> <td style="border: 1px solid black; padding: 5px;">           Signature of Authorized Officer    <b>ROBERT KUNEMUND</b> </td> </tr> </table>			Date of the Actual Completion of the International Search  <b>26 FEBRUARY 1990</b>	Date of Mailing of this International Search Report  <b>30 MAR 1990</b>	International Searching Authority  <b>ISA/US</b>	Signature of Authorized Officer  <b>ROBERT KUNEMUND</b>																							
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